REPORT DOCUMENTATION PAGE	Form Approved OMB NO. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggesstions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any oenalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
11-12-2012	Final Report	6-Apr-2009 - 5-Sep-2012

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Final Report Regarding Surface Chemistry of Nano-Structured Mixed Metal Oxide Films	W911NF-09-1-0130
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 611102
6. AUTHORS	5d. PROJECT NUMBER
Charles Buddie Mullins	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES	8. PERFORMING ORGANIZATION REPORT NUMBER
University of Texas at Austin The University of Texas at Austin 101 East 27th Street Austin, TX 78712 -1539	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) ARO
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 55377-CH.20

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

We have synthesizes and studied nano-structured porous mixed metal oxide thin films with high surface area and catalytic activity. By temporally controlling the deposition of two different metals in low-pressure oxygen we synthesized mixed metal oxide catalytic films with spatially controlled compositions for physical characterization and surface chemical studies. Importantly, mixed metal oxides have desirable catalytic properties; they have been shown to enhance activity and selectivity, as well as reduce sintering.

15. SUBJECT TERMS

mixed-metal oxides, catalysis, nanostructured materials

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Charles Mullins
UU	UU	UU	UU		19b. TELEPHONE NUMBER 512-471-5817

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

Report Title

Final Report Regarding Surface Chemistry of Nano-Structured Mixed Metal Oxide Films

ABSTRACT

We have synthesizes and studied nano-structured porous mixed metal oxide thin films with high surface area and catalytic activity. By temporally controlling the deposition of two different metals in low-pressure oxygen we synthesized mixed metal oxide catalytic films with spatially controlled compositions for physical characterization and surface chemical studies. Importantly, mixed metal oxides have desirable catalytic properties; they have been shown to enhance activity and selectivity, as well as reduce sintering. These materials are expected to have substantial surface areas with high concentrations of surface defects which can enhance adsorption and catalytic activity. We deposited the two metallic components in the oxide films in various time dependent ways to create both spatially homogeneous materials as well spatially heterogeneous materials. We were able to both tune the porous nature and structure of the material as well as the catalytic properties. Our basic research strategy involved: (i) physical characterization as a function of deposition conditions, (ii) study of the adsorption/absorption properties and surface defect concentrations, and (iii) investigation of the surface chemical and catalytic properties of the films, and finally (iv) we also investigated some of these materials as electrodes for the photo-oxidation of water and as anode materials for lithium ion batteries.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
08/01/2011	12.00	David W. Flaherty, Nathan T. Hahn, Allen J. Bard, C. Buddie Mullins, Sean P. Berglund. Photoelectrochemical Oxidation of Water using Nanostructured BiVO4 Films, Journal of Physical Chemistry C, (02 2011): 3794. doi:
08/04/2011	11.00	Sean P. Berglund, C. Buddie Mullins, David W. Flaherty. Selective decomposition of formic acid on molybdenum carbide: A new reaction pathway, Journal of Catalysis, (01 2010): 33. doi:
08/04/2011	8.00	David W. Flaherty, R. Alan May, Sean P. Berglund, Keith J. Stevenson, C. Buddie Mullins. Low Temperature Synthesis and Characterization of Nanocrystalline Titanium Carbide with Tunable Porous Architectures, Chemistry of Materials, (01 2010): 0. doi: 10.1021/cm902184m
09/13/2010	5.00	David W. Flaherty, R. Alan May, Sean P. Berglund, Keith J. Stevenson, and C. Buddie Mullins. Reprint, Chemistry of Materials, (11 2009): . doi:
09/13/2010	6.00	R. Alan May, David W. Flaherty, C. Buddie Mullins, and Keith J. Stevenson. Reprint of J Phys Chem Lett paper, Journal of Physical Chemistry Letters, (03 2010): . doi:
09/13/2010	7.00	Nathan T. Hahn, Heechang Ye, David W. Flaherty, Allen J. Bard, and C. Buddie Mullins. Reprint of ACS Nano paper, ACS Nano, (09 2010): . doi:
12/11/2012	13.00	R. Alan May, David W. Flaherty, C. Buddie Mullins, Keith J. Stevenson. Hybrid Generalized Ellipsometry and Quartz Crystal Microbalance Nanogravimetry for the Determination of Adsorption Isotherms on Biaxial Metal Oxide Films, The Journal of Physical Chemistry Letters, (04 2010): 1264. doi: 10.1021/jz1002428
12/11/2012	19.00	Yong-Mao Lin, Rajaram K. Nagarale, Kyle C. Klavetter, Adam Heller, C. Buddie Mullins. SnO2 and TiO2-supported-SnO2 lithium battery anodes with improved electrochemical performance, Journal of Materials Chemistry, (04 2012): 11134. doi: 10.1039/c2jm16328d
12/11/2012	18.00	William D. Chemelewski, Nathan T. Hahn, C. Buddie Mullins. Effect of Si Doping and Porosity on Hematite’s (alpha-Fe2O3) Photoelectrochemical Water Oxidation Performance, The Journal of Physical Chemistry C, (03 2012): 5255. doi: 10.1021/jp210877u
12/11/2012	17.00	David W. Flaherty, Nathan T. Hahn, R. Alan May, Sean P. Berglund, Yong-Mao Lin, Keith J. Stevenson, Zdenek Dohnalek, Bruce D. Kay, C. Buddie Mullins. Reactive Ballistic Deposition of Nanostructured Model Materials for Electrochemical Energy Conversion and Storage, Accounts of Chemical Research, (03 2012): 434. doi: 10.1021/ar200164u
12/11/2012	16.00	Yong-Mao Lin, Paul R. Abel, Adam Heller, C. Buddie Mullins. alpha-Fe2O3 Nanorods as Anode Material for Lithium Ion Batteries, The Journal of Physical Chemistry Letters, (11 2011): 2885. doi: 10.1021/jz201363j
12/11/2012	15.00	Sean P. Berglund, David W. Flaherty, Nathan T. Hahn, Allen J. Bard, C. Buddie Mullins. Photoelectrochemical Oxidation of Water Using Nanostructured BiVO4, The Journal of Physical Chemistry C, (03 2011): 3794. doi: 10.1021/jp1109459
12/11/2012	14.00	Heechang Ye, David W. Flaherty, Nathan T. Hahn, Allen J. Bard, C. Buddie Mullins. Reactive Ballistic Deposition of alpha-Fe2O3 Thin Films for PhotoelectrochemicalWater Oxidation, ACS Nano, (04 2010): 1977. doi: 10.1021/nn100032y
12/28/2009	3.00	David W. Flaherty, Sean Berglund, and C. Buddie Mullins. New Reprint - 140. David W. Flaherty, Sean Berglund, and C. Buddie Mullins, “Selective decomposition of formic acid on molybdenum carbide: A new reaction pathway,” J. Catal. 269, 33-43 (2010). , Journal of Catalysis, (12 2009): . doi:

TOTAL: 14

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
08/31/2009	1.00	D.W. Flaherty, A. May, K. J. Stevenson, C. B. Mullins. Manuscript submitted to journal "Chemistry of Materials.", Chemistry of Materials ( )
08/31/2009	2.00	C. B. Mullins. Selective Decomposition of Formic Acid on Molybdenum Carbide: A New Reaction Pathway, Journal of Catalysis ( )
12/28/2009	4.00	R. Alan May, David W. Flaherty, C. Buddie Mullins, Keith J. Stevenson. Manuscript - Generalized ellipsometry / quartz crystal microbalance nanogravimetric porosimetry of anisotropic TiO_2, Applied Physics Letters (12 2009)

TOTAL: **3**

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Wen-Yueh Yu	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
C. Buddie Mullins	0.05	
FTE Equivalent:	**0.05**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Final Report: Surface Chemistry of Nano-Structured Mixed Metal Oxide Films
PRINCIPAL INVESTIGATOR: C. B. Mullins, University of Texas at Austin
PREPARED FOR: Dr. Jennifer J. Becker, U. S. Army Research Office

Statement of Problem: We synthesized and studied nano-structured porous mixed metal oxide thin films with high surface area and catalytic activity. By temporally controlling the deposition of two different metals in low-pressure oxygen we synthesized mixed metal oxide catalytic films with spatially controlled compositions for physical characterization and surface chemical studies. Importantly, mixed metal oxides have desirable catalytic properties; they have been shown to enhance activity and selectivity, as well as reduce sintering. These materials are expected to have substantial surface areas with high concentrations of surface defects which can enhance adsorption and catalytic activity. We deposited the two metallic components in the oxide films in various time dependent ways to create both spatially homogeneous materials as well spatially heterogeneous materials. We were able to both tune the porous nature and structure of the material as well as the catalytic properties.
Our basic research strategy includes: (i) physical characterization as a function of deposition conditions, (ii) study of the adsorption/absorption properties and surface defect concentrations, and (iii) investigation of the surface chemical and catalytic properties of the films, and finally (iv) we also investigated some of these materials as electrodes for the photo-oxidation of water and as anode materials for lithium ion batteries.

Summary of the Most Important Results:
In one study nanostructured $BiVO_4$ films were synthesized by coevaporation of bismuth and vanadium in an oxygen ambient, a process referred to as reactive ballistic deposition (RBD). The films were tested in various electrolyte solutions to assess their activity for photoelectrochemical water oxidation. Deposition parameters, including the V/Bi atomic flux ratio and the incident angle of deposition, were adjusted. Films deposited with excess vanadium (V/Bi = 2) and incident angles of deposition at 65□ showed the highest initial photocurrents with IPCE values above 21% for light wavelengths of 340-460 nm (in 0.5 M Na_2SO_4 at 1.0 V vs Ag/AgCl). With continued illumination the excess vanadium in these films dissolved into the electrolyte and the photocurrents dropped by 60-75% before reaching steady state. The steady-state photocurrent and IPCE values
(above 14% for 340-460 nm light) were higher than the initial values for films synthesized with stoichiometric amounts of vanadium and bismuth (V/Bi = 1) and incident angles of deposition at 65□. Stoichiometric $BiVO_4$ films remained stable under illumination but their photocurrents were limited by surface reaction kinetics. The addition of cobalt as an electrocatalyst to the surface of these films increased their photocurrent by a factor of 3.

In another study we reported the preparation of □alpha-Fe_2O_3 electrodes using a technique known as reactive ballistic deposition in which iron metal is evaporatively deposited in an oxygen ambient for photoelectrochemical (PEC) water oxidation. By manipulating synthesis parameters such as deposition angle, film thickness, and annealing temperature, we find that it is possible to optimize the structural and morphological properties of such films in order to improve their PEC efficiency. Incident photon to current conversion efficiencies (IPCE) are used to calculate an AM1.5 photocurrent of 0.55 mA/cm2 for optimized films with an IPCE reaching 10% at 420 nm in 1 M KOH at □0.5 V versus Ag/AgCl. We also note that the commonly observed low photoactivity of extremely thin hematite films on fluorine-doped tin oxide substrates may be improved by modification of annealing conditions in some cases.

We also studied selective decomposition of formic acid since it is important as a prototype to study selective bond cleavage of oxygenates. We demonstrated that carbon-modified Mo(1 1 0), C–Mo(1 1 0), is up to 15 times more selective for the dehydrogenation of formic acid than Mo(1 1 0). Reflection absorption infrared spectroscopy (RAIRS) indicates that carbidic carbon blocks active sites for C–O bond cleavage, decreasing the rate of dehydration. Steady-state reactive molecular beam scattering (RMBS) shows that dehydration is the dominant reaction pathway on clean Mo(1 1 0), while C–Mo(1 1 0) selectively promotes dehydrogenation. Kinetic analysis of RMBS data reveals that formic acid dehydrogenation on Mo(1 1 0) has an activation energy of 34.4 ± 3.3 kJ mol□1 while the C–Mo(1 1 0) surface promotes distinct pathways for dehydrogenation with an activation energy of only 12.8 ± 1.0 kJ mol□1. RAIRS spectra suggest the new pathways include the formation of monodentate formate, and at temperatures of 500 K and greater,

direct activation of the C–H bond to form carboxyl, both of which decompose via a COd
2 intermediate
to evolve CO_2 and H_2.

High surface area, porous titanium carbide films were also synthesized at room temperature via reactive ballistic deposition (RBD). X-ray diffraction and X-ray photoelectron spectroscopy show that evaporative deposition of titanium in an ethylene ambient environment allows for low temperature (35 C) synthesis of nanocrystalline titanium carbide, a material which typically requires high processing temperatures to produce. Angle-dependent RBD allows for the controlled tuning of TiC nanostructure and porosity where changing the deposition angle from near normal incidence (13) to more glancing angles (50-85) changes the film morphology from relatively nonporous, dense TiC to a continuous, reticulated TiC and finally to discrete, nanocolumnar TiC. The influence of the deposition angle on TiC optical constants, porosity, specific surface area, and the pore size distribution has been investigated using hybrid quartz crystal microbalance and ellipsometric porosimetry. Notably, TiC films deposited at 35 C at an angle of 70 have a specific surface area of 710 m2 3 g-1 and a mean Kelvin radius of 1.8 nm, making them attractive materials for application in catalysis, energy conversion, and storage.

We combined generalized ellipsometry and quartz crystal nanogravimetry to determine adsorption isotherms and changes in the optical properties
of biaxial TiO_2 thin films by monitoring changes in the Mueller matrix. Individual Mueller matrix elements, corresponding to a variety of polarization states, exhibit dramatically different sensitivities to the adsorption of toluene. While some elements are sensitive to structural anisotropy and orientation, others report uniquely on the refractive index. The fast (na) optical axis reflects the greatest change in refractive index due to the adsorption, leading to a decrease from $\Delta n_{800nm}=0.4$ to 0.1. This change is discussed in terms of the Bragg-Pippard (B-P) effective medium approximation, which is shown to accurately describe changes in optical behavior in response to adsorption. The integration of generalized ellipsometry with quartz crystal nanogravimetry establishes a highly sensitive technique for acquiring adsorption isotherms and for chemical optical sensing of structurally anisotropic thin films.

We also hydrothermally synthesized single-crystalline hematite (α-Fe_2O_3) nanorods and investigated them as an anode material for Li-ion batteries. Electrodes prepared with this material exhibited initial reversible capacities of 908 mAh g1 at 0.2 C rate and 837 mAh g1 at 0.5 C rate, and these capacities were completely retained after numerous cycles. The α-Fe_2O_3 nanorods average 40 nm in diameter and 400 nm in length providing a short path for lithium-ion diffusion and effective accommodation of the strain generated from volume expansion during the lithiation/delithiation process.

We also studied the photoelectrochemical water oxidation performance under simulated solar irradiation of hematite (α-Fe_2O_3) films synthesized by coevaporation of pure Si and Fe in an oxygen ambient, a process known as reactive ballistic deposition, is studied as a function of Si doping level and film porosity, ranging from dense films to nanocolumnar films. It is found that Si segregates to the hematite surface, does not improve the bulk conductivity, and lowers the optical absorption coefficient. Nevertheless, the photoelectrochemical performance of Si-doped, porous films is significantly improved relative to undoped, porous films. However, the improvement relative to dense, undoped films is marginal. It is concluded that Si acts to passivate the hematite surface and aids charge transfer to the solution. Additionally, from incident photon conversion efficiency measurements it is found that Si doping and porosity have little effect on the normalized spectral response of 100 nm thick hematite films.

Finally, Li-ion battery anodes made of SnO_2 nanoparticles and a TiO_2-supported SnO_2 nanocomposite formed of equimolar amounts of the Sn and Ti oxides were investigated, respectively. By limiting the voltage window of the charge/discharge cycles to the range 50 mV–1.0 V, both the SnO_2-based anode and the SnO_2/TiO_2-based anode show improved cycling stability. Compared to the SnO_2 nanoparticle based anodes, the TiO_2-support-SnO_2 nanocomposite anodes exhibit better cyclability and higher Coulombic efficiency. During the first lithiation process, Li+ conducting Li_xTiO_2 is formed in the SnO_2/TiO_2 composite, which structurally/mechanically supports the electrode. The anode made of amorphous TiO_2-cassiterite SnO_2 retained a reversible capacity of 500 mAh g 1 (based on the weight of SnO_2) or 320 mAh g 1 (based on the weight of SnO_2/TiO_2) at 0.2 C after 100 cycles and at a rate as fast as 5 C retained a stable reversible capacity of 340 mAh g 1 (based on the weight of SnO_2) or 220 mAh g 1 (based on the weight of SnO_2/TiO_2).

Bibliography

1. David W. Flaherty, Sean P. Berglund, and C. Buddie Mullins, “Selective decomposition of formic acid on molybdenum carbide: A new reaction pathway,” J. Catal. 269, 33-43 (2010). http://dx.doi.org/10.1016/j.jcat.2009.10.012

2. David W. Flaherty, R. Alan May, Sean P. Berglund, Keith J. Stevenson, and C. Buddie Mullins, “Low temperature synthesis and characterization of nanocrystalline titanium carbide with tunable porous architectures” Chem. Mater. 22, 319-329 (2010). http://dx.doi.org/10.1021/cm902184m

3. R. Alan May, David W. Flaherty, C. Buddie Mullins, and Keith J. Stevenson, “Hybrid generalized ellipsometry and quart crystal microbalance nanogravimetry for the determination of adsorption isotherms on biaxial metal oxide films,” J. Phys. Chem. Lett. 1, 1264-1268 (2010). http://dx.doi.org/10.1021/jz1002428

4. Nathan T. Hahn, H. Ye, David W. Flaherty, Allen J. Bard, and C. Buddie Mullins, “Reactive Ballistic Deposition of α-Fe_2O_3 Thin Films for Photoelectrochemical Water Oxidation,” ACS Nano 4, 1977-1986 (2010). http://dx.doi.org/10.1021/nn100032y

5. Sean P. Berglund, David W. Flaherty, Nathan T. Hahn, Allen J. Bard, and C. Buddie Mullins, “Photoelectrochemical Oxidation of Water using Nanostructured $BiVO_4$ Films,” J. Phys. Chem. C 115, 3794-3802 (2011). http://dx.doi.org/10.1021/jp1109459

6. Yong-Mao Lin, Paul R. Abel, Adam Heller, and C. Buddie Mullins, “α-Fe_2O_3 nanorods as anode material for lithium ion batteries,” J. Phys. Chem. Lett. 2, 2885-2891 (2011). http://dx.doi.org/10.1021/jz201363j

7. David W. Flaherty, Nathan T. Hahn, Sean M. Berglund, Yong-Mao Lin, R. Alan May, Keith J. Stevenson, Zdenek Dohnalek, Bruce D. Kay, and C. Buddie Mullins, “Reactive ballistic deposition of nanostructured model materials for electrochemical energy conversion and storage,” Acc. Chem. Res. 45, 434-443 (2012). http://dx.doi.org/10.1021/ar200164u

8. William D. Chemelewski, Nathan T. Hahn, and C. Buddie Mullins, “The effect of Si doping and porosity on Hematite’s (-Fe_2O_3) photoelectrochemical water oxidation performance,” J. Phys. Chem. C 116, 5255-5261 (2012). http://dx.doi.org/10.1021/jp210877u

9. Yong-Mao Lin, Rajaram K. Nagarale, Kyle C. Klavetter, Adam Heller, and C. Buddie Mullins, “A fast and stable TiO_2-supported SnO_2 nanocomposite lithium ion battery anode,” J. Mater. Chem. 22, 11134-11139 (2012). http://dx.doi.org/10.1039/c2jm16328d

Technology Transfer